

Detection with x-ray fluorescence of Ni silicides or precipitates in solid phase crystallized Si

Claudine Chen¹, Scott Mc Hugo², and Harry Atwater¹

¹Thomas J. Watson Laboratories of Applied Physics, California Institute of Technology, Pasadena, CA 91125, USA

²Advanced Light Source, Ernest Orlando Lawrence Berkeley National Laboratory,
University of California, Berkeley, California 94720, USA

INTRODUCTION

The drive for high cell efficiency at lower cost in photovoltaics has stimulated research into thin-film silicon technology coupled with low-cost substrates, such as soda-lime or borosilicate glass. The low thermal stability (<650 °C) of these glasses has motivated low temperature approaches for making crystalline Si thin films. A promising process for application in low-cost thin-film crystalline silicon solar cells is selective nucleation and solid phase epitaxy (SNSPE) of Si with Ni nanoparticles as nucleation seeds. To make a polycrystalline layer thick enough to fabricate a solar cell, a sub-micron thick template layer is first made by SNSPE, and an active light absorbing Si layer several microns thick is epitaxially deposited on the template. Metal-induced crystallization of amorphous Si with Ni has been shown to occur below 600 °C [1,2], making it compatible with the use of conventional soda-lime glass substrates, and with growth rates much faster than other metal-induced crystallization with In and Al, or for unseeded growth. However Ni that is not stabilized in silicides has high diffusivity and high solubility in Si even at 600 °C, which could potentially result in Ni precipitates that act as shunts or carrier recombination centers in a solar cell. With the x-ray fluorescence (XRF) microprobe, we can assess whether Ni precipitates at the grain boundaries and in the bulk may be a serious problem or not for cell performance.

EXPERIMENT

Two types of samples, which have been crystallized by Ni were analyzed. A photolithographically patterned thin film of 75 nm thick a-Si was implanted with Ni into lithographically defined nucleation areas with a dose of $5 \times 10^{16} \text{ cm}^{-2}$ and annealed at 600 °C incrementally to characterize the crystallization process. Also, a 100 nm thick a-Si layer was nucleated by Ni particles randomly distributed on the surface and annealed at 600 °C for 1-2 hours. A 5 μm thick epitaxial layer was grown on the thin template layer by molecular beam epitaxy at 600 °C substrate temperature at a rate of 0.3 nm/s. Cross sections were made of the sample.

RESULTS AND DISCUSSION

With vacuum annealing, seeded crystallization began at the Ni nucleation areas and continued by nickel mediated crystallization by fast propagation of branching needle-like crystalline structures, thought to be led by silicide particles [2], which produced <110> textured substrates. Transmission electron microscopy analyses showed a large grain size but a high density of sub-grain boundary defects in the crystallized Si film. For the samples nucleated with Ni particles, a fully crystallized sample was used as a template for Si epitaxial deposition of a 5 μm thick Si film. Transmission electron microscopy analysis showed a strong microstructural correlation between the substrate grain structure and the grain structure in the deposited layer, indicating local epitaxial growth. The final layer exhibited a large-grain morphology, with grain sizes larger than 4 μm .

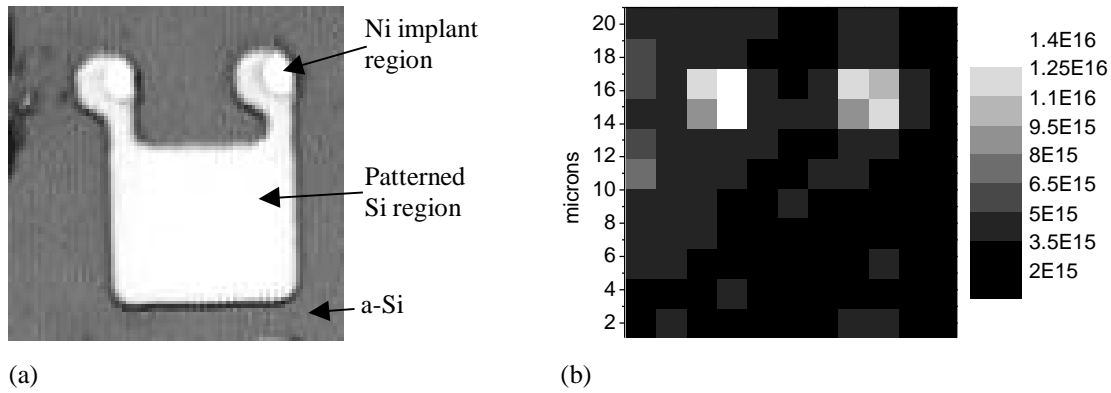


Fig. 1. (a) Optical image, and (b) x-ray fluorescence map of Ni dose, of a patterned Si structure with Ni implanted in 2 μm diameter seed regions with dose of $5 \times 10^{16} \text{ cm}^{-2}$. This sample was annealed at 600 $^{\circ}\text{C}$ for an hour, and the Si region is fully recrystallized.

The detection limit for Ni for the x-ray fluorescence microprobe is approximately $1 \times 10^{14} \text{ cm}^{-2}$. The solubility of Ni in Si at the anneal temperature of 600 $^{\circ}\text{C}$ is $3 \times 10^{14} \text{ cm}^{-3}$ [3], and is the maximum concentration for dissolved Ni in Si. For a plan view sample of the photolithographically patterned samples with Ni-implanted nucleation sites, the Ni dose would be $2.25 \times 10^9 \text{ cm}^{-2}$ at the solubility limit, which is too low to detect with XRF. If Ni collected at the grain boundaries or at the amorphous-crystalline growth interface as has been seen in high resolution TEM [2], the precipitates should be detected if larger than 60 nm cubed, which is an estimate of the smallest NiSi_2 precipitate that can be detected. However, there was no inhomogeneity in the Ni distribution outside of the Ni implant regions. In a sample annealed at 600 $^{\circ}\text{C}$ for an hour, a strong signal of $1 \times 10^{16} \text{ cm}^{-2}$ was seen in the implanted regions, and the background Ni dose was $4 \times 10^{15} \text{ cm}^{-2}$, even outside of the patterned Si. The dose is above that of the maximum dissolved Ni concentration, which suggests that there is a uniform distribution of Ni precipitates.

REFERENCES

1. Z. Jin, G. A. Bhat, M. Yeung, H. S. Kwok and M. Wong, *J. Appl. Phys.* **84**, 194-200 (1998).
2. C. Hayzelden and J. L. Batstone, *J. Appl. Phys.* **73**, 8279-8289 (1993).
3. E. R. Weber, *Appl. Phys. A* **30**, 1-22 (1983).

This work was supported by the National Renewable Energy Laboratory under subcontract AAD-9-18668-03 under the U.S. Department of Energy Contract No. DEAC36-99-G010337.

Principle investigator: Harry A. Atwater, Email: haa@caltech.edu. Telephone: 626-395-2197.
Contact also: Claudine Chen, Email: ming@caltech.edu. Telephone: 626-395-3826.